

Conclusions

Our results give additional support to the proposed mechanisms for the formation of recoil products from hydrocarbons. Three primary species, ^{11}C , ^{11}CH , and $^{11}\text{CH}_2$, all uncharged, appear to be responsible for the products formed in these systems. The reactions involved seem to be formally analogous to insertion reactions into C-H and C=C bonds initially forming activated complexes. These can become stabilized through energy transfer to the solvent cage, can react further to form "buildup" products, or can undergo decomposition forming labeled molecules or radicals. The simplest mode of decomposition involves rupturing the β C-C bonds to give C_2 fragments. The C_2 products formed from those fragments were studied

extensively. Products, such as C_3 , etc., formed by more complicated modes of decomposition were not determined since they were present in only relatively small amounts. The yields of C_2 products from various liquid hydrocarbons were shown to be related to the structures of the parent molecules, indicating that C-H bonds are indeed the sites at which the reactions occur. The results are in agreement with earlier proposals that the activation energies for insertion reactions involving these primary species are nearly zero.

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The Photochemical Reaction of Hydrogen Peroxide with Allyl Alcohol-3,3- d_2

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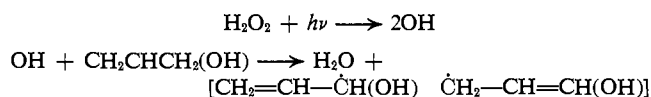
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The reaction of hydroxyl radicals, derived from the photolysis of hydrogen peroxide, with allyl alcohol-3,3- d_2 in the frozen state at 77°K. and in liquid solutions in the range 253–350°K. has been studied. An analytical method based on the gas phase reaction of water with sodium mirrors has been developed. For the reaction with sodium, the isotopic separation factor for protium and deuterium in water was found to be 1.8 in the range of 0–35% deuterium. For all the photochemical experiments, abstraction of deuterium atoms was shown to occur with $8.4 \pm 2.5\%$ of the hydroxyl radicals formed; the remainder was considered to add to the olefinic bond. Electron spin resonance spectra of irradiated frozen samples showed that absorption of light by the deuterated allyl alcohol leads to cleavage of the carbon-oxygen bond and that the reaction of hydroxyl radicals with the alcohol is consistent with the interpretation that deuterium atoms are abstracted.

Introduction

Photochemical studies of ultraviolet-irradiated hydrogen peroxide in aqueous solutions of allyl alcohol at 0–50° have shown that the principal mechanism is the addition of hydroxyl radicals to the olefinic bond.¹ Evidence for this has also been obtained by Dixon and Norman² in electron spin resonance studies of the reaction of hydroxyl radicals, formed by the reaction of titanous ion with hydrogen peroxide, with aqueous allyl alcohol. Electron spin resonance studies of ultraviolet-irradiated solutions of hydrogen peroxide in allyl alcohol in the glassy state at about 90–120°K. indicate that hydroxyl radicals abstract an α -hydrogen

atom from the alcohol.^{3–5} Thus the reactions



yield α -hydroxyallyl radical.

It seemed somewhat surprising to us that abstraction would not occur at about room temperature whereas it would occur at about 100°K., even after allowance is made for the widely different conditions of the glassy state and the liquid aqueous solution. We have, therefore, investigated this seeming anomaly by a tracer technique using allyl alcohol which has both α -hydrogen atoms replaced by deuterium atoms. The principle of the method depends upon the formation of deuterium-containing water by abstraction of deuterium atoms with hydroxyl radicals. In order to analyze the products of the reaction, we have developed a method based on the reaction of gaseous water with sodium mirrors. Details of this method and the determination of separation factors for protium and deuterium on solid sodium are reported here. We have also obtained some supporting evidence from electron spin resonance studies with allyl alcohol-3,3- d_2 .

Experimental Section

Materials. Hydrogen peroxide (90%), Becco Chemical Division, was used without further purification. Allyl alcohol, Fisher Certified Reagent, was purified by fractional distillation. Allyl alcohol-3,3- d_2 was syn-

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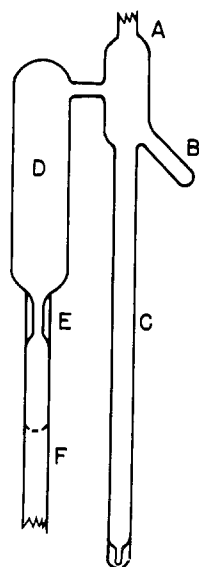


Figure 1. Apparatus for the reaction of water with sodium mirrors.

thesized for us by Merck Sharp and Dohme of Canada and was used as received.

Photochemical Method. Samples for irradiation were prepared according to our technique of micro-photochemistry.⁶ The quartz reaction cells, 5 cm. long, 1.0-mm. i.d., and 0.25-mm. wall thickness, contained about 4.0 μ l. of reaction solution. In our earlier work we have described the filling of the reaction tubes by means of a microsyringe with the usual metal needle. Because hydrogen peroxide may decompose on metal surfaces, in the present work the metal needle was removed, and the glass end of the syringe was drawn to a fine point to serve as a substitute needle.

Except at 77°K., where temperature was maintained by liquid nitrogen, temperature control was effected by a stream of dry nitrogen brought to the desired temperature by heat-exchange systems using liquid nitrogen, solid carbon dioxide, and electrical resistance heating. Irradiation was carried out with a high-pressure mercury arc of British Thomson-Houston manufacture. The light was focused by a quartz lens through a Vycor filter. Spectra obtained with this arrangement showed broadening of the resonance line to give virtually a continuum in the region 2400–2900 Å. with no emission in the region 2530–2730 Å. because of self-reversal.

Irradiation was carried out in duplicate; one sample was reserved for deuterium analysis while the second was tested for residual peroxide. Normally irradiation was continued until all the peroxide had decomposed, but at 77°K. some remained. Residual peroxide was analyzed iodometrically, the reaction tube having been crushed under 25 ml. of water to liberate the sample for titration.

Deuterium Analysis. Deuterium content was determined by treating the vaporized reaction sample with a sodium mirror to yield molecular hydrogen which was subsequently analyzed by gas chromatography. The sodium reaction apparatus is shown in Figure 1. A piece of freshly cut sodium was placed in

F, which was then sealed off as indicated by the dotted line, and the vessel was attached to a high-vacuum line through a ground glass joint at A. The reaction cell was placed with its end in the well at the bottom of C. The vessel was evacuated, sodium was distilled onto the walls of D, and the vessel was sealed off at the constriction E to separate it from undistilled sodium. The evacuated vessel was isolated from the vacuum system, and the reaction was initiated by breaking the photochemical reaction cell with a glass-enclosed magnetic hammer which had been stored in B. The reaction was allowed to proceed for several hours, after which the hydrogen produced was transferred through a liquid nitrogen trap to a gas buret, using combined mercury-diffusion and Toepler pumps. The gas buret was connected to a gas sampling loop of a gas chromatography apparatus, and a measured gas sample could thus be introduced into the carrier gas stream.

The chromatographic technique used was similar to that of Moore and Ward.⁷ Separation was achieved on a 20-ft. copper column packed with alumina coated with ferric oxide to maintain ortho-parahydrogen equilibrium and not allow spin isomer separation which would mask HD. The packing material was prepared according to the method of Carter and Smith.⁸ The column was operated in a liquid nitrogen bath at 77°K. with helium as the carrier gas. The helium was prepurified by passage through a 4-ft. column of activated alumina at 77°K. As katharometer detection systems have poor sensitivity for hydrogen in helium as carrier gas, the hydrogen was converted to water by passing through a 15-in. column of 30–40 mesh copper oxide at 650°. The system was thus able to detect 0.1 μ mole of hydrogen.

The chromatographic system was calibrated by injecting samples containing H₂, HD, and D₂. D₂ was prepared by the reaction of deuterium oxide with sodium. HD was prepared by the reaction of deuterium oxide with lithium aluminum hydride. Cylinder hydrogen was added to the mixture and the exact composition was determined by mass spectrometer.

Electron Spin Resonance. The spectrometer system, irradiations, and observations were very much as described previously.^{5,9} Irradiations were carried out at 77°K. by keeping the sample tube in a Varian liquid nitrogen quartz dewar insert. Higher temperatures, at which some observations were made, were obtained by use of a Varian variable temperature accessory. Two light sources were used: a low-pressure mercury resonance arc housed in Vycor from which the transmitted light was chiefly 2537 Å. as Vycor is opaque to 1849-Å. light; and a high-pressure mercury arc with a Pyrex 0-53 glass filter which eliminated radiation shorter than 2800 Å.

Results and Discussion

Chromatography. With the conditions given above, H₂, HD, and D₂ were readily separated on the chromatographic column and detected as water after reaction with cupric oxide. The same linear calibration of peak areas held for the three species. This is at

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variance with the results reported by Venugopalan and Kutshcke¹⁰ who found slightly different sensitivities for each constituent. They also observed slight deviations from linearity for very small quantities, below 0.4 μ mole.

Reaction of Vapors with Sodium. It is known that when liquid water^{11,12} or gaseous water¹³ reacts with sodium the hydrogen produced is depleted in the heavier isotope compared to the original water. For water vapor, experiments at but a single concentration have been reported.¹³ As knowledge of the relationship between deuterium content of the evolved gas and original water was necessary for our analytical method, we have used our technique to examine the relationship between the evolved gas and the composition of water over a range of concentration. Refractive index measurements made with a differential refractometer were used to determine the deuterium content of the liquid water samples.¹⁴ The results are shown in Figure 2. For the linear portion of the plot, up to about 35% deuterium in liquid, the separation factor defined by

$$\alpha = (n_1/n_2)_{\text{gas}}/(n_1/n_2)_{\text{liq}}$$

was found to be 1.8, where n_1 and n_2 represent the number of protium and deuterium atoms, respectively. This separation factor is identical with that found by Horiuti and Szabo using water containing 1.8% deuterium.

For the experiments represented in Figure 2 sodium was in excess. The ratio of moles of gas, determined by gas buret measurements, to moles of water used was found to be 0.51 ± 0.006 . As the theoretical ratio should be 1:2 based on the reaction



this is good evidence that the reaction of water vapor with sodium mirrors proceeds to completion.

Photochemical Reaction. The results of the photochemical experiments are summarized in Table I.

Table I. Photochemical Reaction of Hydrogen Peroxide with Allyl Alcohol^a

Temp., Irrad., °K. hr.	H ₂ O ₂ dec., %	Hydrogen evolved in analysis, %			Abstraction, %	
		H ₂	HD	D ₂	Max.	Min.
77 40	91.3	93.3	6.7	0	10.2	6.4
253 4	100	93.2	6.8	0	9.4	5.9
298 2	100	92.2	7.8	0	10.8	6.8
350 2	100	92.2	7.8	0	10.8	6.8

^a H₂O₂, 35.8 μ moles; H₂O, 9.4 μ moles; CH₂CHCD₂(OH), 44.2 μ moles.

Except for the reaction at 77°K., no peroxide was detected at the termination of irradiation. Also no gaseous products were formed on irradiation except at 77°K. where 1.3 μ moles of gas was liberated. Experi-

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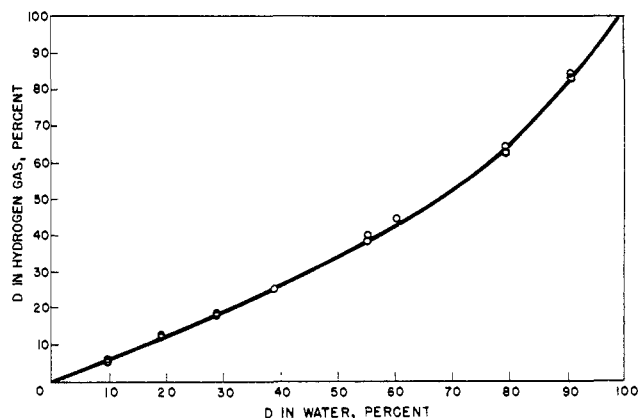


Figure 2. Deuterium content of hydrogen gas formed by reaction of deuterium-enriched water with sodium.

ments performed in the absence of hydrogen peroxide showed that no deuterium-containing hydrogen was evolved after prolonged irradiation.

Where all of the peroxide has been decomposed and no gaseous products have been formed, it may be assumed that all of the hydroxyl radicals from H₂O₂ have either added to the olefinic bond or abstracted α -hydrogen, in this case, deuterium atoms. The resulting mixture should, therefore, contain unreacted allyl alcohol, various hydroxylated allyl alcohol derivatives, and water. As the hydroxylated products will have extremely low vapor pressures and as the stoichiometry and separation factors for the reaction of allyl alcohol with sodium is not known, a precise determination of the fraction of the reaction which proceeds by abstraction was not possible. It is, however, possible to estimate the maximum and minimum contributions of abstraction. It can be assumed that the reaction of sodium with ROH when R is not H is given by



Thus it is to be expected that fractionation of hydrogen isotopes will not occur with allyl alcohol or hydroxylated derivatives. A definite maximum for abstraction can then be obtained if the separation factor we have obtained for water is used. A minimum may be obtained on the assumption that no fractionation occurs in the reaction with sodium. On this basis the results we have obtained may be expressed as $8.4 \pm 2.5\%$ over the entire range studied. This calculation will also hold for the solid sample at 77°K. after allowance is made for residual peroxide and some decomposition of peroxide to form oxygen.

From the results obtained in this study it may be deduced that the activation energies for abstraction of α -hydrogen or addition to the olefinic bond of allyl alcohol by hydroxyl radical are about the same. In view of the fact that activation energies for addition to olefinic bonds may be quite low, this indicates that the abstraction reaction very likely has a correspondingly low activation energy. Indeed for the ratio of abstraction rate to addition rate to be temperature independent, without invoking a fortuitous exactness, the activation energies should be nearly zero. This is not too improbable, particularly when the large exothermicity of the abstraction reaction is considered;

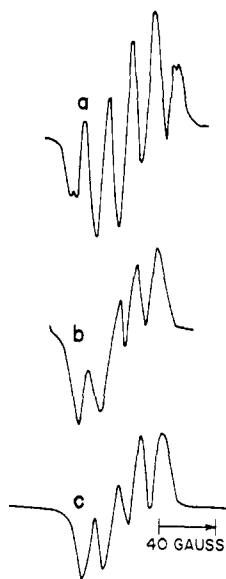


Figure 3. Electron spin resonance spectra derived from allyl alcohol: (a) irradiated at 77°K. with the resonance arc, spectrum taken at 103°K.; (b) irradiated at 77°K. with the resonance arc, spectrum taken at 132°K.; (c) sample contains H₂O₂ (irradiated at 77°K. with the high-pressure arc through a Pyrex filter), spectrum taken at 128°K.

not only is the bond strength of the product H-OH very high, 120 kcal., but additional exothermicity is gained from the resonance energy of allylic radical, 12.6 kcal.¹⁵

The abstraction reaction was not invoked in earlier work at room temperature on the photochemical reaction¹ or in electron spin resonance studies² in aqueous solutions. Detection in either case would have been difficult. In the first case, abstraction would not have been clearly evident from the product analysis; in the second case, the principal free radicals present were those resulting from addition to the olefinic bond, and thus radicals resulting from abstraction would have been masked.

Electron Spin Resonance. The electron spin resonance spectra we have obtained confirm the interpretation of our earlier work in frozen systems.⁵ This work showed that direct irradiation of allyl alcohol at 77°K. gave evidence for cleavage of the carbon-oxygen bond with the formation of allyl radical. On warming the sample to about 120°K. after irradiation, the spectrum of α -hydroxyallyl radical was identified. We have explained this by assuming that OH radicals formed at 77°K. abstract α -hydrogen atoms from allyl alcohol as the temperature is raised slightly. Mixtures of hydrogen peroxide and allyl alcohol when irradiated with light which could be absorbed only by the peroxide did not yield allyl radical but only hydroxyallyl radical. For comparison with the deuterated allyl alcohol, we have now repeated this work and the results are shown in Figure 3. Corresponding results with the deuterated compound are shown in Figure 4. The five-line spectrum in Figure 3 is indicative of the allyl radical while the four-line spectrum is indicative of

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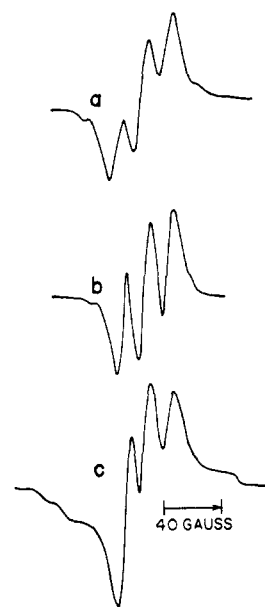


Figure 4. Electron spin resonance spectra derived from allyl alcohol-3,3-d₂: (a) irradiated at 77°K. with the resonance arc, spectrum at 77°K.; (b) irradiated at 77°K. with the resonance arc, spectrum at 119°K.; (c) sample contains H₂O₂ (irradiated at 77°K. with the high-pressure arc through a Pyrex filter), spectrum taken at 119°K.

hydroxyallyl radical as they represent the interaction of four and three protons, respectively, with the unlocalized electron of the resonating radical. As the splitting is about 14 gauss, substitution of deuterium atoms for proton should yield hyperfine interaction of less than 2 gauss, which would not be detectable in this system. It would be predicted, therefore, that analogous spectra from allyl alcohol-3,3-d₂ would consist of three lines as hyperfine interaction would occur with two protons for either allyl or hydroxyallyl radicals. The spectra of Figure 4 are in agreement with this prediction as only three-line spectra were found. A fuller discussion of the principles involved in this argument is given in our earlier papers.^{5,9}

As the tracer experiments show that at 77°K. the major portion of hydroxyl radicals adds to the olefinic bond, it is not obvious why the free radicals which presumably would be formed are not observed in electron spin resonance experiments. A possible explanation for this is that these alkyl radicals are not formed, but that hydroxyl radicals, which are formed in pairs, add in pairs; alternatively, photoactivated hydrogen peroxide may add to the double bond without yielding free hydroxyl radicals. There appears to be, in any case, a very marked cage effect in the solid systems at 77°K. as the results in Table I show that decomposition of hydrogen peroxide is not complete after very prolonged irradiation.

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